

Highly Active Fenton-Like Catalyst Derived from Solid Waste-Iron Ore Tailings Using Wheat Straw Pyrolysis

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1 Highly active Fenton-like catalyst derived from solid waste-iron ore
2 tailings using wheat straw pyrolysis

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10 **Abstract:** The pollutants degradation rate of iron ore tailings-based heterogeneous
11 catalysts is the main factor limiting its application. Herein, an iron ore tailings-based
12 Fenton-like catalyst(I/W(3:1)-900-60) with relative fast catalysis rate was constructed
13 by co-pyrolysis(900 °C, 60min holding time) of iron ore tailings and wheat straw with
14 mass ratio of 3:1. With wheat straw blending, the generated I/W(3:1)-900-60 presented
15 a larger surface area(24.3 m²/g), smaller pore size(3.707 nm), reduced iron species (Fe²⁺
16 from magnetic) and a higher catalytic activity(0.0229 min⁻¹) than I-900-60 (1.196 m²/g,
17 12.935 nm, 0.012 min⁻¹) pyrolyzed using a single iron ore tailings under the same
18 pyrolysis conditions. In addition, biochar and iron ore tailings in I/W(3:1)-900-60 were
19 tightly combined through chemical bonding. The optimal catalyst remains active after
20 three cycles, indicating its catalytic stability and recyclability. The good Fenton-like
21 MB degradation efficiency of I/W(3:1)-900-60 was ascribed to the sacrificial role of
22 biochar, as well as the electron transfer between biochar and iron active sites or the

23 redox cycles of $\equiv\text{Fe}^{3+}/\text{Fe}^{2+}$. This finding provides a facile construction strategy for a
24 highly active iron ore tailings-based Fenton-like catalyst, and thereby had a great
25 potential application in wastewater treatment.

26 **Key words:** Iron ore tailings; Wheat straw; Heterogeneous catalyst; Biochar;
27 Decomposition rate

28 **1. Introduction**

29 Mining industry is an important activity to extract mineral products around the
30 world. Nevertheless, the mining process always brings a certain degree of pollution.
31 Tailings are solid waste remaining after mining valuable minerals, which are usually
32 disposed at waste dams or landfills that present potential environmental damage (Rico
33 et al. 2008; Kossoff et al. 2014). In March 2020, a miserable accident involving a waste
34 dam occurred when the Yichun waste dam (Harbin, China) for the storage of iron ore
35 tailings collapsed. This accident caused 60,000 m³ of mining tailings disclosing and 3
36 million m³ of wastewater releasing, leading to 70 kilometers of river pollution and
37 serious economic loss. A number of other tailings dam accidents have occurred in
38 different countries (Batista et al. 2020) . According to statistics (Yi et al. 2020), the
39 accumulated of tailings were about 207 billion tons in China, of which the total amount
40 of tailings produced in 2018 was about 12.11 billion tons. Among all types of tailings,
41 iron ore tailings have the largest amount of production, about 4.76 billion tons,
42 accounting for about 39.31% of the total tailings production (Huang et al. 2020).

43 Therefore, it is imperative to explore new technologies for reducing iron ore
44 tailings and their reuse as raw materials to produce value-added products. Recently, a
45 promising application of iron ore tailings is its utilize as adsorbents or catalysts to
46 remove dye compounds (Silva et al. 2011; Augusto et al. 2018), e.g. as a
47 raw/regenerated efficient Fenton and Fenton-like catalysts for wastewater treatment.
48 Given the high iron contents observed in iron ore tailing, it is reasonable to assume that
49 these wastes are good catalysts for Fenton or Fenton-like processes (Augusto et al.

2018). However, Fe^{2+} is the effective state for activating the oxidant, while the most common state in iron waste is Fe^{3+} (dos Santos et al. 2016), and the presence of Fe^{3+} modifies the degradation rate (reaction time as long as 24 h) of substance. Some researchers got significant progress in trying to enhance the pollutant oxidation rate through reducing Fe^{3+} to Fe^{2+} (Augusto et al. 2018; de Freitas et al. 2019). Freitas *et al* achieved good results (80% dye decomposed with 3 h reaction) for the oxidation of methylene blue when iron ore tailing pretreated in a CH_4 atmosphere at 550 °C for 2 h.

Better degradation results could be achieved in case of iron waste pretreatment under reducing atmosphere (H_2 , CO , CH_4). Biomass could produce reducing gases and compounds during pyrolysis (Williams and Besler 1996; Wang et al. 2010). In our previous paper, we found that a unite mass wheat straw could produce about 5 mg/g H_2 and 18 mg/g CH_4 (Gao and Goldfarb 2019). Therefore, if iron tailings and wheat straw blends were pretreated through pyrolysis to realize the conversion of ferric iron to a low-valent state, it would not only improve the catalytic oxidation efficiency of organic matter, but also realize the resource utilization of wheat straw, which is of great significance.

Therefore, this paper applies methylene blue as a model pollutant to investigate the influence of pyrolysis conditions on the catalyzed degradation rate of pollutants. The pyrolyzed products' morphology, physical-chemical properties, stability and the catalytic mechanism were discussed. The research in this article aims to provides a theoretical basic for iron ore tailing catalyst with high degradation rate.

2 Materials and methods

72 2.1 Materials

73 Iron ore tailings were kindly provided by “Hainan mining” industry, located in
74 Hainan, China. The sample was hematite tailings (T), and ground to 74 μm prior to use.
75 Wheat straw selected as biomass because of the high production in China, which was
76 ground in a coffee mill and sieved to a particle size between 100 and 300 μm (Gao and
77 Goldfarb 2019). Table S1 showed the characteristics of wheat straw and hematite
78 tailings. Methylene blue was purchased from Aladdin Chemical Reagent Co.Ltd. China.

79 2.2 Synthesis of the catalysts

80 Hematite tailings and wheat straw mixed with mass ratio 1:1, 2:1, 3:1, 4:1 and 5:1.
81 Then, these mixtures were treated in tube furnace using a heating rate of 10 $^{\circ}\text{C}$
82 /min(Wang *et al* found feedstock pyrolyzed at this heating rate could produce more
83 reducing gas, such as CO and H₂) (Wang et al. 2018) until different temperatures (500,
84 600, 700, 800 and 900 $^{\circ}\text{C}$) for different holding times (30, 45, 60, 90 and 120 min). The
85 obtained catalyst was denoted as I/W(a:b)-T-t, where I iron ore tailings, W wheat straw,
86 a:b the mass ratio (w/w), T finally temperature, t holding time.

87 2.3 MB decomposition experiments

88 To evaluate the decomposition rate of catalyst produced from iron ore tailings, the
89 bath catalytic experiments were carried out using 0.3 g of pyrolyzed product in contact
90 with 100 mL dye solution with initial concentration of 60 mg/L and 16 mmol H₂O₂
91 under a shaker. 1.5 mL of solution was pipetted at given time intervals, centrifuged for
92 1 min and the dye concentration was detected by a UV-vis spectrophotometer (Unico

93 UV-2800) at 664 nm.

94 To investigate the stability and reusability of catalyst, the optimal pyrolyzed
95 product was reused/recycled several times for the MB decomposition under the same
96 Fenton-like condition.

97 2.4 Analytical method

98 The phase transformation of ferrochemical group in pyrolyzed solid was analyzed
99 by XRD (Bruker D8 Advance, Germany). The morphology and composition were
100 characterized by SEM-EDX (FEI Quanta™ 250, USA). The textural properties were
101 test by BET (BELSORP-max, Japan). The functional groups of catalysts were
102 investigated by FTIR (Bruker Vertex 80v, Germany). Electron paramagnetic resonance
103 (EPR, Bruker 300E spectrometer, Germany) was applied to test the main reactive
104 oxidative species (ROS) generated in the system. Fe valence and carbon functional
105 group variation of catalysts were characterized by XPS (Thermo Fisher Escalab 250 Xi,
106 USA), and the C1s1/2(284.6 eV) was used as the binding energy calibration standard.

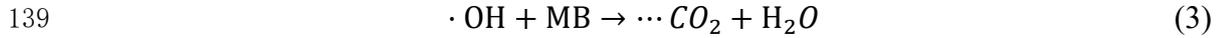
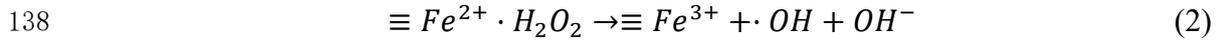
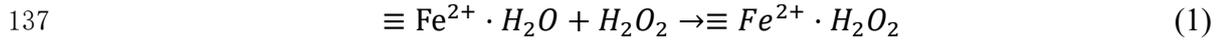
107 **3 Results and discussion**

108 3.1 Determination of optimal pyrolysis based on degradation rate

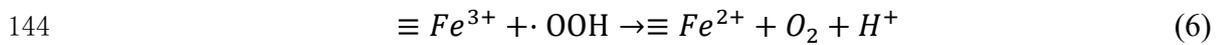
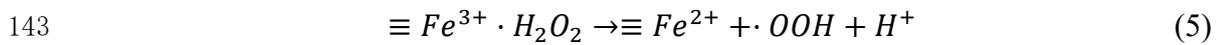
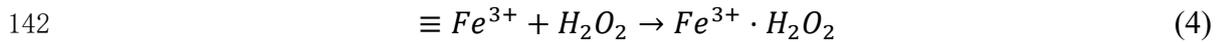
109 The pyrolysis preparation mass ratio (iron ore tailings to wheat straw), reaction
110 time and heating rate were fixed at 3:1, 60 min and 10 °C/min, respectively, and
111 catalysts were obtained under different pyrolysis temperature. Fig.1(a) showed the
112 comparison of MB removal efficiency versus time and pseudo-second-order kinetic
113 constant (k_2 , $R^2 > 0.994$) under different catalysts, which -5 min means the H₂O₂ was
114 added after 5min adsorption. Only approximately 20% of MB was removed after 1 h

115 with a kinetic rate of 0.0139 min^{-1} when the product prepared at $500 \text{ }^\circ\text{C}$ used. However,
116 the removal rate and efficiency were substantially improved as the pyrolyzed
117 temperature increased. The best decomposition rate (0.0182 min^{-1}) and efficiency (74%)
118 were reached using a catalyst prepared at $900 \text{ }^\circ\text{C}$, which was much higher than the
119 generated iron ore tailings catalyst reported by Augusto *et al* ($7.4 \times 10^{-4} \text{ min}^{-1}$, 63%)
120 (Augusto et al. 2018). Considering the dye decomposition rate and efficiency, the
121 optimal pyrolysis temperature for synthesizing catalyst was determined to be $900 \text{ }^\circ\text{C}$.

122 Setting the pyrolysis temperature as $900 \text{ }^\circ\text{C}$ and final holding time as 60 min and
123 heating rate as $10 \text{ }^\circ\text{C}/\text{min}$, the removal efficiency and rate of MB were investigated by
124 pyrolysis products at different mass ratio. As shown in Fig.1(b), only 10% MB was
125 removed with a removal rate k_2 of 0.0120 min^{-1} when the product prepared by hematite
126 tailings only, indicating that the pyrolyzed product synthesized from iron ore tailings
127 might not be active for dye degradation. While the decomposition efficiency of MB (k_2
128 increased from 0.0120 min^{-1} to $0.0182/0.0183 \text{ min}^{-1}$) gradually increased when the
129 products made from hematite tailings and wheat straw blends were used as catalyst.
130 This may be due to biomass blends helped to reduce the $\equiv\text{Fe}^{3+}$ to $\equiv\text{Fe}^{2+}$ or low-valent
131 iron (Ellison and Boldor 2021). The mechanism of H_2O_2 activation by iron ore tailings
132 based catalyst with $\equiv\text{Fe}^{2+}$ may involve the following reaction processes(Luo et al. 2010).
133 Firstly, a complex assigned as $\equiv\text{Fe}^{2+} \cdot \text{H}_2\text{O}_2$ may form between the hydrous surface of
134 $\equiv\text{Fe}^{2+} \cdot \text{H}_2\text{O}$ and H_2O_2 (Eq.(1)), where $\equiv\text{Fe}^{2+} \cdot \text{H}_2\text{O}$ represents the reduced sites on the
135 iron ore tailings catalyst surface. The formed $\equiv\text{Fe}^{2+} \cdot \text{H}_2\text{O}_2$ can produce $\cdot\text{OH}$ by H_2O_2
136 activation, which is ready to decompose and oxidize MB(Eq.(2) and (3)).



140 However, the radical formation mechanism by $\equiv Fe^{3+}$ and H_2O_2 is proposed as
 141 follows:

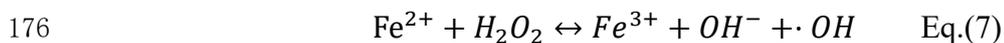


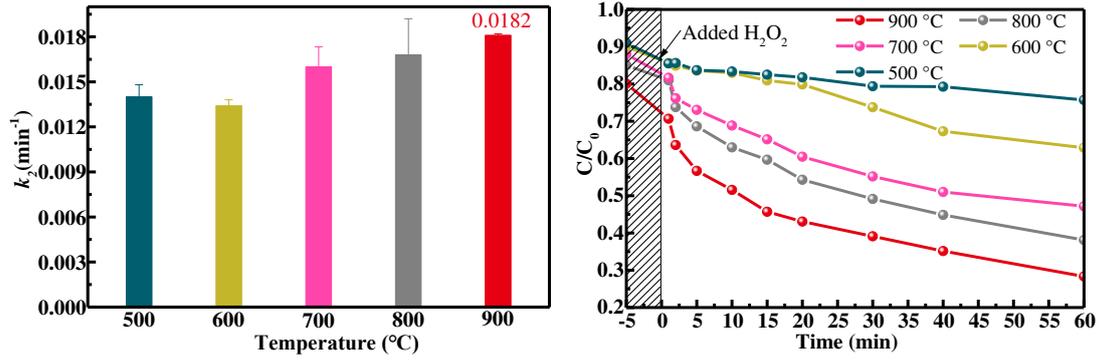
145 The formed $\equiv Fe^{2+}$ subsequently produce $\cdot OH$ (Eq.(1)-(3)). Although $\cdot OH$ can
 146 be generate from H_2O_2 when either $\equiv Fe^{2+}$ or $\equiv Fe^{3+}$ is present, the generation rates are
 147 much faster between $\equiv Fe^{2+}$ and oxidant (Kwan and Voelker 2002). Although the
 148 degradation efficiency for catalysts produced from mass ratio 1:1, 2:1 and 3:1 was
 149 equivalent, degradation rate k_2 values of mass ratio 3:1(0.0182 min⁻¹) and 2:1 (0.0183
 150 min⁻¹) were higher than 1:1(0.0158 min⁻¹). In order to realize the iron ore tailings bulk
 151 utilization and construct a catalyst with higher degradation rate, we determined the
 152 optimal mass ratio of iron ore tailings to wheat straw was 3:1.

153 Fixing the pyrolysis temperature as 900 °C, the ratio of iron ore tailings to wheat
 154 straw as 3:1 and heating rate as 10 °C/min, the optimum holding time was investigated
 155 in Fig.1(c). The dye decomposition efficiency of pyrolyzed product was enhanced when
 156 the holding time for the synthesis catalyst stretched from 30 to 60 min. However, the
 157 degradation efficiency of MB was not significantly improved when the holding time
 158 further extended to 90 and 120 min. Interestingly, k_2 showed a first increasing then

159 decreasing trend as the holding time extending, and reached the maximum (0.0182 min⁻¹)
160 when the holding time was 60 min. Thus, 60 min was the optimal catalyst holding
161 time among those investigated parameters.

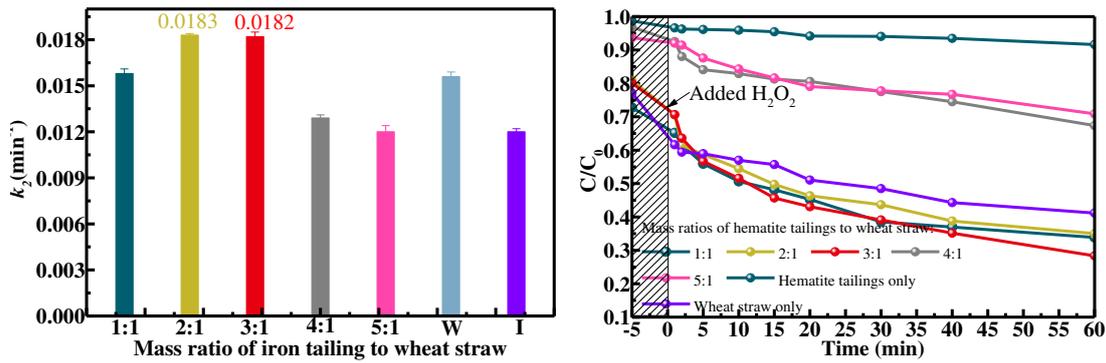
162 To sum up, the relative optimal pyrolysis condition was a blends ratio of 3:1, a
163 pyrolysis temperature of 900 °C and a holding time of 45 min. pH as an important factor
164 for the efficiency of Fenton-like reaction, the effect of pH was investigated in Fig 1(d).
165 We could see that pH could significantly affect the degradation of MB in iron ore
166 tailings catalyzed Fenton-like process. As shown in Fig.1(d), the degradation efficiency
167 was relatively low and the k_2 values were 0.0104 min⁻¹ and 0.0182 min⁻¹ at pH 8.1 and
168 6.8(did not adjust). While the decomposition of MB gradually increased as the pH value
169 decreasing and got a highest/fastest degradation efficiency (84% MB removal, 0.0229
170 min⁻¹) at around pH 3, which was consistent with previous studies (Hu et al. 2011). The
171 generation of $\cdot OH$ from H₂O₂ is the key step in the entire Fenton-like process,
172 and $\cdot OH$ catalyzed by iron ore tailings are gradually limited with pH increasing. The
173 higher pH with more OH⁻ will cause the reaction (Eq. (7)) to shift back and reduce the
174 activity of Fenton reagent (Zheng et al. 2016), which resulted in a slow decomposition
175 rate of I/W(3:1)-900-60.





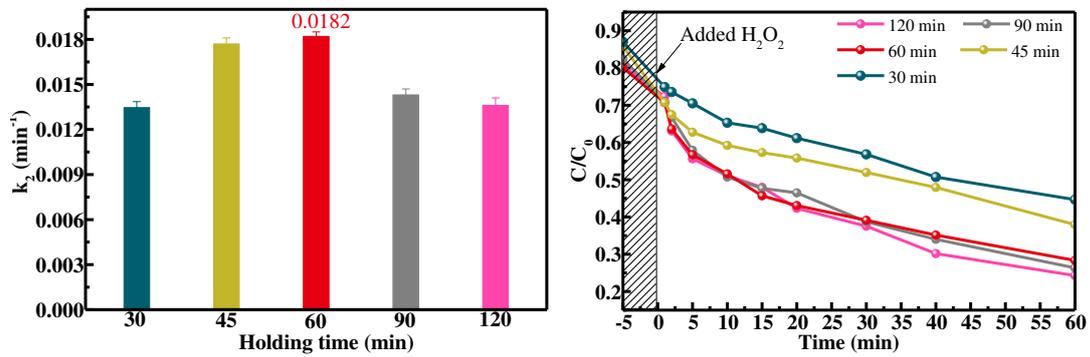
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(a) Pyrolyzed temperature



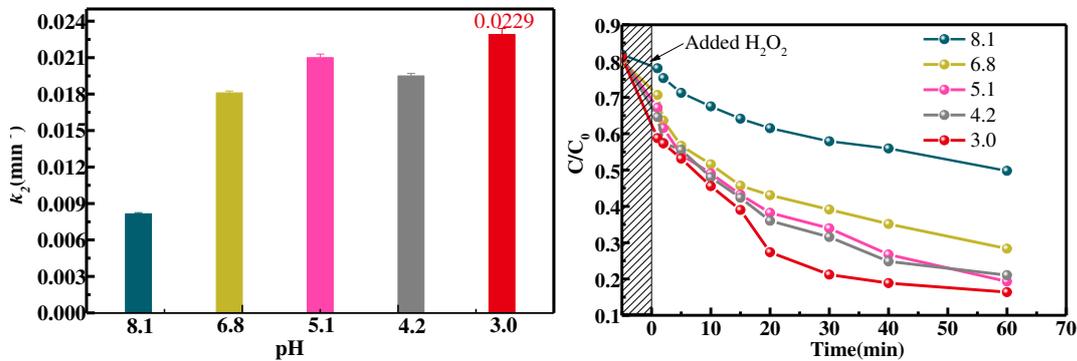
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(b) Iron ore tailings to biomass mass ratio



181
182

(c) Holding temperature



183
184

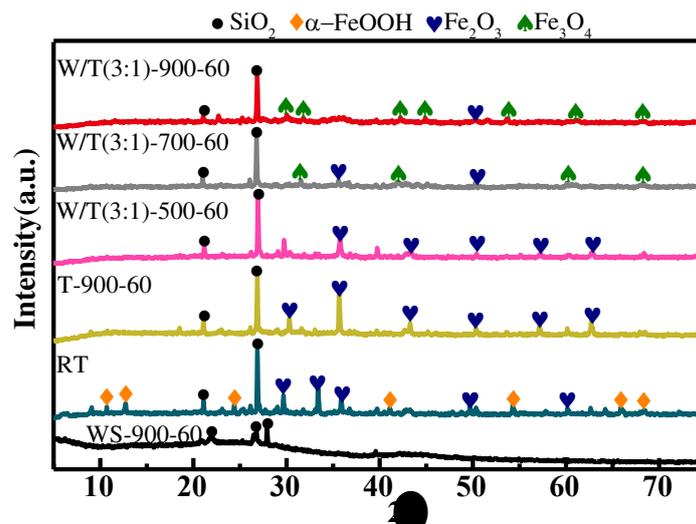
(d) pH value

Figure 1 Degradation of MB by pyrolyzed product prepared under different conditions

185

186 3.2 Catalyst characterization

187 Since the catalytic efficiency was apparently different by I-900-60, WS-900-60
 188 and I/W(3:1)-900-60, XRD patterns were collected to indicate the phase information of
 189 these samples, shown in Fig.2. The XRD pattern of I/W(3:1)-900-60 showed diffraction
 190 peaks at $2\theta=30.3^\circ$, 43.3° , 53.8° , 57.5° , 68.2° corresponded to Fe_3O_4 , which exhibits
 191 magnetic characteristics. The peaks of WS-900-60 were noted at $2\theta=21.8^\circ$, 26.5° , 28.0° ,
 192 corresponding to SiO_2 crystallites. The diffraction peaks of raw iron ore tailings (RT)
 193 were attributed to $\alpha\text{-FeOOH}$, and $\alpha\text{-FeOOH}$ was converted to Fe_2O_3 when heated to
 194 900°C under N_2 atmosphere (Zhang et al. 2018). Therefore, only the pyrolysis of iron
 195 ore tailings or wheat straw cannot produce a composite with low-valent iron.



196
 197 Figure 2 XRD patterns of the raw and prepared samples

198 Significant transformation of Fe_2O_3 to Fe_3O_4 was observed at $700\text{-}900^\circ\text{C}$. When
 199 the temperature reached above 700°C , most of Fe_2O_3 peaks disappeared, and the
 200 diffraction peaks of magnetite appeared. It can be concluded that Fe_2O_3 with trivalent
 201 could be reduced to Fe_3O_4 during high-temperature pyrolysis. More Fe_2O_3 spindles
 202 were converted to Fe_3O_4 as the temperature increasing. This might due to that there
 203 were organic matters such as cellulose, hemicellulose and lignin in wheat straw, and

204 these organic matters could be cracked and devolatilized into reducing gas or liquid,
 205 such as H₂, CH₄, which lead to the ferric iron reduction (Gong et al. 2012; Sharma et
 206 al. 2015; Xun et al. 2019; Yunji et al. 2019). In summary, in the process of co-pyrolysis
 207 of wheat straw and iron ore tailings, the reducing substances such as H₂ or CH₄
 208 produced from wheat straw exhibited strong reducibility to reduce iron ore tailings to
 209 magnetite. Furthermore, the reduction degree increased as temperature increasing.

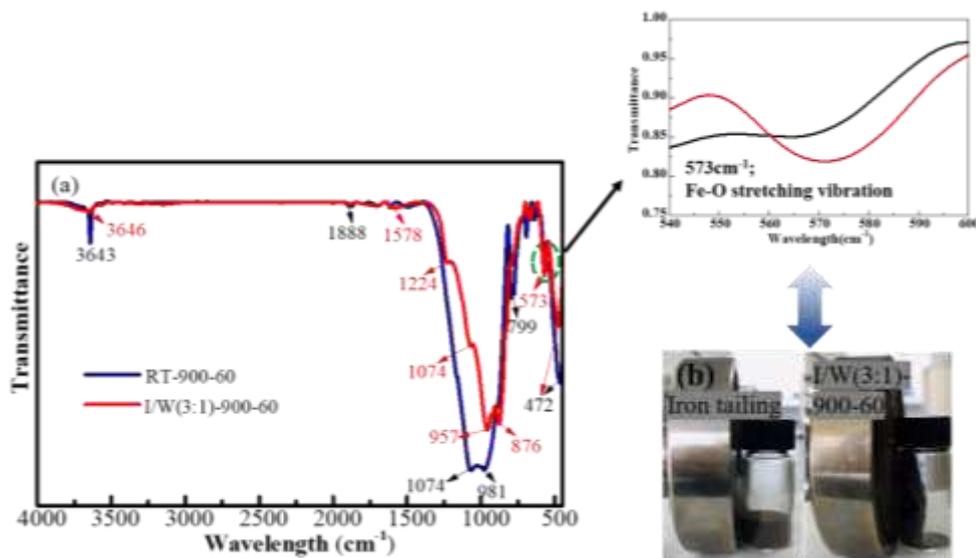
210 To illustrate the effect of biomass/wheat straw on the high degradation efficiency
 211 catalyst formation, the morphologies of I-900-60 and I/W(3:1)-900-60 were further
 212 compared. The surface morphologies of I-900-60 and I/W(3:1)-900-60 were shown in
 213 Fig.S1. The I-900-60 presented a large flaky structure with a flat and non-porous
 214 surface after pyrolysis, mainly because the natural structure of iron ore tailings. In the
 215 case of I/W(3:1)-900-60, SEM images showed that most particles had a smaller flake
 216 structure, with porous surface. This result indicated that mixing wheat straw promote
 217 the formation of a porous and smaller flake structure.

218 Table 1 BET and BJH results of prepared catalysts

Samples	Surface area(m ² /g)	Pore volume(cc/g)	Average pore size(nm)
I-900-60	1.1963	0.2749	12.935
I/W(3:1)-900-60	24.319	5.5875	3.707

219 As observed from SEM images, I/W(3:1)-900-60 had a smaller particle than I-
 220 900-60. N₂ adsorption-desorption isotherm was applied to calculate the surface area,
 221 pore volume and pore size distribution. As shown in Table 1 and Fig.S2, the average
 222 pore size of T-900-60 and I/W(3:1)-900-60 was 12.95 nm and 3.707 nm. However, the
 223 total pore volume was 0.2749 cc/g and 5.5875 cc/g, respectively. Thus, we can conclude
 224 that wheat straw addition increased the pore volume, and decreased average pore size.

225 Additionally, although I/W(3:1)-900-60 had a much larger specific surface area(24.319
 226 cm^2/g) than I-900-60(1.1963 cm^2/g), its surface area was smaller than those reported
 227 iron-load activated carbon adsorbent (300-600 m^2/g) (Park et al. 2015; He et al. 2016;
 228 Saleh et al. 2017). This result further verified that prepared catalysts from iron ore
 229 tailings had weak adsorption ability. Therefore, we speculated the MB degradation by
 230 I/W(3:1)-900-60 was due to catalysis instead of adsorption. I/W(3:1)-900-60, with
 231 relatively larger surface area and richer pore volume, could provide greater active
 232 catalysis sites and increase catalysis performance (Neamtu et al. 2004; Duarte et al.
 233 2012), agreed with the improved MB degradation efficiency catalyzed by I/W(3:1)-
 234 900-60.



235
 236 Figure 3 (a) the photos of the products attraction to a magnetic device; (b) FTIR spectra of I-900-
 237 60 and I/W(3:1)-900-60

238 There is an important question to further discuss that whether composites (wheat
 239 straw biochar and iron ore tailings) were simply mixed and exist alone or integrated
 240 together. Fig.3(a) showed the catalysts were attracted as a whole by a magnetic device,
 241 indicating iron ore tailings and biochar combined as a whole. This binding form is

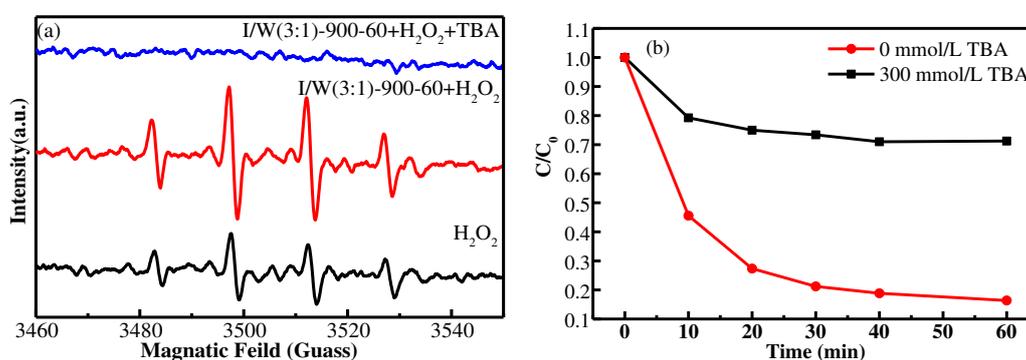
242 beneficial to remove the catalyst from wastewater after reaction. In addition, FTIR
243 spectra was shown in Fig.3(b). The peak at 3643/3646 cm^{-1} was attributed to O-H
244 stretching and bending vibrations (Zhang et al. 2018). Similar I-900-60 peaks were
245 observed in the spectra of both I-900-60 and I/W(3:1)-900-60, including Si-O stretching
246 vibrations of the Si-O-Si, Si-O-Al, Si-O-Fe groups (1074 cm^{-1} , 957/981 cm^{-1} , 472 cm^{-1}),
247 although their intensities varied (Doelsch et al. 2003). The silicon content in iron ore
248 tailings was much higher than that in wheat straw (Table S1). Therefore, the intensity
249 of Si-O stretching vibration in I-900-60 was stronger than in the spectrum of I/W(3:1)-
250 900-60. Meanwhile, new peaks associated with the -C=O and -C-H stretching vibration
251 at 1224 cm^{-1} and 876 cm^{-1} were observed in the spectrum of I/W(3:1)-900-60; these
252 peaks were assigned mainly to the formation of small organic molecules (such as,
253 phenol, furfural, styrene) that are devolatilized, oxidized or creaked from wheat straw
254 during pyrolysis process. In addition, a new peak at 573 cm^{-1} attributed to an
255 asymmetric Fe-O stretching vibration was observed. It might be caused by loading iron
256 into biochar or Fe_3O_4 itself (Yuan and Dai 2014). Therefore, the new bond Fe-O on
257 I/W(3:1)-900-60 may indicate the combination of iron and biochar occurred through
258 chemical bonds.

259 3.3 The catalyst's stability and reusability analysis

260 It is important to evaluate the stability of a heterogeneous catalyst. As illustrated
261 in Fig.S3, I/W(3:1)-900-60 was stable in first three runs and remained high MB
262 degradation efficiency. At the 4th run, the activity of I/W(3:1)-900-60 reduced slightly
263 but the degradation efficiency still higher than 80%, showing the iron ore tailings based

264 catalyst can be reused for at least 4 Fenton-like cycles without significant activity loss.
 265 This slightly activity loss is probably due to the small molecules produced during MB
 266 degradation occupying part of the active sites, leading to a decrease in catalytic
 267 efficiency (Zhang et al. 2018). In addition, the concentration of leaching iron ions after
 268 first three runs was measured. As shown in Table S2, the concentration of leached iron
 269 was 0.089 mg/L, 0.085 mg/L, and 0.093 mg/L, which was only 0.8% of the iron content
 270 in I/W(3:1)-900-60. Low leached iron concentration also indicated heterogenous
 271 Fenton catalysis was the dominant reaction for MB removal (Gao et al. 2017).
 272 Meanwhile, XRD and SEM were applied to examine the structure stability of I/W(3:1)-
 273 900-60. As illustrated in Fig.S4, compared with fresh catalyst, the crystalline nature and
 274 morphology of used I/W(3:1)-900-60 did not change significantly. These results
 275 indicated that the cost-effective I/W(3:1)-900-60 was a promising heterogenous catalyst
 276 in Fenton-like catalytic degradation of organic wastewater due to its significant stability
 277 and reusability.

278 3.4 Reactive oxidative species and catalysis mechanism



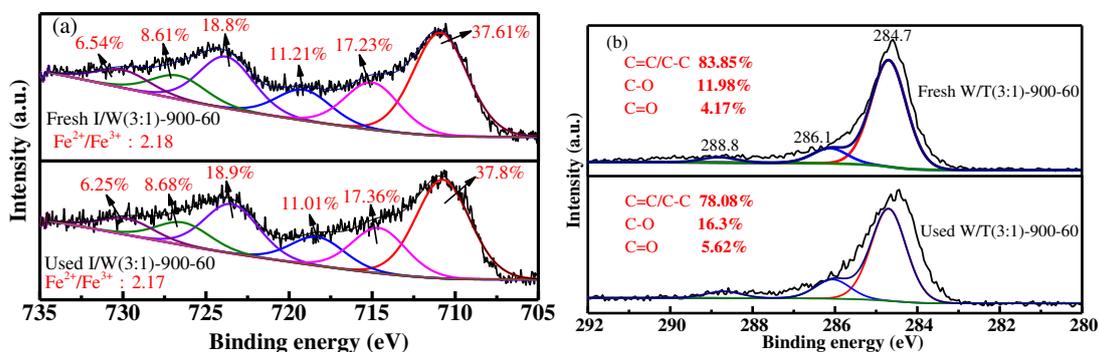
279
 280 Figure 4 (a)DMPO-ROS adducts generated from I/W(3:1)-900-60 Fenton catalysis reactions
 281 at 10min (b)influence of radical scavenger (TBA) on the catalytic degradation of MB

282 ROS produced in I/W(3:1)-900-60 was detected by an EPR spin-trap technique

283 with DMPO. Fig.4(a) showed the EPR spectrum of the generated adducts during the 10
284 min reaction. On the EPR spectrum, there was observed a four-fold peak with an
285 intensity of 1:2:2:1, which was labeled to the DMPO-OH (Yang et al. 2013). However,
286 the four-fold peak was not appeared in the presence of 300 mmol/L T-Butyl alcohol
287 (TBA, \cdot OH scavenger). Therefore, \cdot OH was the key ROS produced in I/W(3:1)-900-
288 60 catalyzed Fenton-like reactions. Fig.4(b) showed the effect of \cdot OH on MB
289 degradation. We can see the removal efficiency of MB significantly decreased from 84%
290 to 29% in the presence of 300 mmol/L. This result indicated that \cdot OH played a dominant
291 role in MB degradation in I/W(3:1)-900-60 catalyzed Fenton-like reactions.

292 The electron exchange between Fe(II)/Fe(III) and H₂O₂ can induce the formation
293 of \cdot OH in the heterogeneous Fenton-like reaction. XPS was applied to analyze the
294 chemical state of iron species on I/W(3:1)-900-60 before and after catalysis reaction.
295 Fig. 5 shows XPS results of Fe2*p* in fresh and used I/W(3:1)-900-60. The peaks located
296 at 724.8 eV and 710.9 eV were attributed to Fe 2*p*_{1/2} and Fe 2*p*_{3/2} states of Fe2*p* orbits,
297 respectively (Gao et al. 2017; Li et al. 2018). Furthermore, the Gaussian-Lorentzian
298 was applied to decompose these two peaks into 6 different fitting peaks(Ding; et al.
299 2016). Among them, the fitting peaks located at 719.1 and 729.9 eV attribute to satellite
300 peaks, as well as at 712.0 and 725.3 eV assign to Fe³⁺, and at 710.6 and 723.8 eV
301 correspond to Fe²⁺, respectively (Li et al. 2018). A summary of deconvoluted peaks'
302 area and the Fe²⁺/Fe³⁺ ratio was presented in Fig.5(a). Apparently, the ratio value of
303 Fe²⁺/Fe³⁺ decreased from 2.18 to 2.17 after reaction, demonstrating only a small amount
304 of \equiv Fe²⁺ lost electrons and oxidized to \equiv Fe³⁺ during the catalysis reaction. These XPS

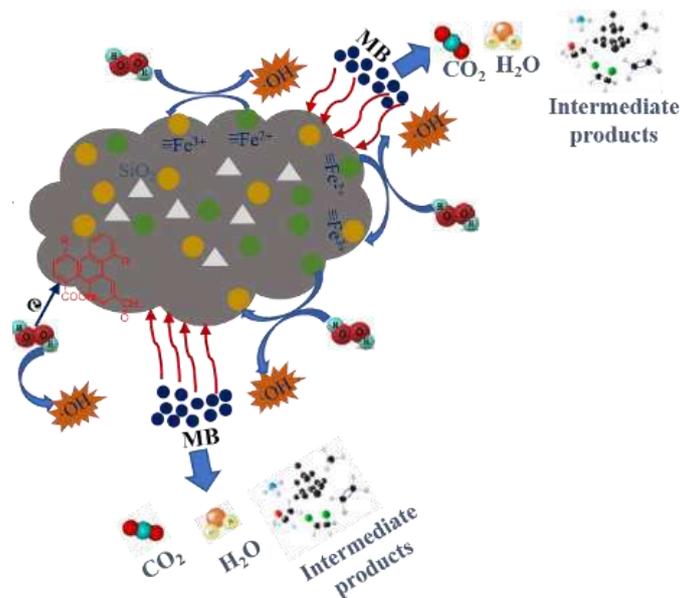
305 results are in accordance with the good recyclability and stability of I/W(3:1)-900-60
 306 catalyst, which may attribute to the protective effects of the biochar (Li et al. 2018).



307
 308 Figure 5 XPS spectra of Fe 2p(a) and C1s(b) on I/W(3:1)-900-60 before and after catalysis
 309 reaction

310 To further verify the protective role of biochar during Fenton-like reaction. XPS
 311 analysis was conducted to investigate the functional groups changes of I/W(3:1)-900-
 312 60 catalyst. As illustrated in Fig.5(b), the C1s spectra can be decomposed into three
 313 fitting peaks with C=C sp²/C-Csp³ (284.7 eV), C-O (286.1 eV) and C=O (288.8 eV) (Li
 314 et al. 2017b). Apparently, compared with the fresh I/W(3:1)-900-60, the relative content
 315 of C=C sp²/C-Csp³ carbon was reduced by 5.8%, C-O and C=O increased by 4.4% and
 316 1.4% after catalysis reaction. This indicates that biochar was oxidized during the
 317 Fenton-like process with turning C=C sp²/C-Csp³ carbon to C-O or C=O. Therefore,
 318 the recyclability and stability of I/W(3:1)-900-60 catalyst may owe to the existence of
 319 biochar which acted as a sacrificial role and limited the oxidation of iron active sites in
 320 catalyst. Actually, the biochar can act as a catalyst with electron donor-accepter for the
 321 induction of H₂O₂ into •OH or •OOH. The persistent free radicals (PFRs) on the
 322 surface of biochar formed by the thermal decomposition of organic compounds can be
 323 the reduced and oxidized active sites through electron transfer to form radical species
 324 ((Khachatryan and Dellinger 2011; Zhu et al. 2018). Fang *et al* found that PFRs on the

325 surface of biochar have an important influence on the production of OH by H₂O₂
 326 activation (Fang et al. 2014). In addition, the PFRs on the biochar surface lead to the
 327 existence of unpaired electrons, which can exchange electrons directly with organic
 328 matter, accelerating the MB degradation efficiency (Fang et al. 2013; Yang et al. 2016).



329
 330 Figure 6 Proposed mechanism for Fenton catalysis reaction of I/W(3:1)-900-60

331 According to the above analysis results and discussion, the possible Fenton-like
 332 reaction mechanism was illustrated in Fig. 6. At the beginning, the MB molecules were
 333 adsorbed onto biochar of I/W(3:1)-900-60 from aqueous solution through surface
 334 action and pore diffusion. Then, the iron active sites of ≡Fe²⁺ and PFRs in biochar
 335 simultaneously transfer electron to H₂O₂ to generate ·OH for MB degradation.
 336 Moreover, the electron transfer between PFRs and iron active sites or the redox cycles
 337 of ≡Fe³⁺/Fe²⁺ combined results in the enhanced degradation efficiency and rate of
 338 heterogenous Fenton-like reaction. Significantly, the stable performance of I/W(3:1)-
 339 900-60 with good reusability is due to the sacrificial effect of biochar for limiting the
 340 oxidation of iron active sites. In addition, the presence of unpaired electrons in PFRs

341 contributes to a certain extent to improve the degradation efficiency of pollutants. Table
 342 2 showed the MB decompose rate k_2 for various Fenton-like catalysts. We can see that
 343 I/W(3:1)-900-60(0.0229 min^{-1}) exhibited a higher k_2 than or comparable to most
 344 reported kinetic rate data, which indicates that the co-pyrolysis of iron ore tailings and
 345 biomass waste is an effective way to improve the degradation rate/efficiency of iron ore
 346 tailings based heterogeneous catalysts. Meanwhile, it is of great significant to realize
 347 the resource utilization of iron ore tailings. However, these kinetic rate dates are far less
 348 than the degradation rate of homogeneous Fenton catalysis (Gou et al. 2021). Thus, the
 349 performance optimization of iron ore tailings-based heterogeneous catalysts based on
 350 porous and low-valent iron still needs further studied.

351 Table 2 Comparison of MB removal by Fenton-like methods with different catalysts

Catalyst	MB (mg/L)	Catalyst dosage (g/L)	Time (min)	k (min^{-1})	Reference
I/W(3:1)-900-60	60	3	60	2.29×10^{-2}	This study
Fe_3O_4	100	3	30	1×10^{-3}	(Costa et al. 2008)
$\text{Fe}_3\text{O}_4/\text{H}_2/300/1\text{h}$	100	3	30	4×10^{-3}	(Costa et al. 2008)
$\text{Fe}_3\text{O}_4/\text{H}_2/400/1\text{h}$	100	3	30	2×10^{-2}	(Costa et al. 2008)
Ferrocene	10	0.372	120	6.17×10^{-3}	(Wang et al. 2014)
$\text{Fe}_3\text{O}_4/\text{rGO}$	10	0.3	120	2.6×10^{-3}	(Liu et al. 2013)
$\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{C}$	50	1	140	3.6×10^{-2}	(Liu et al. 2013)
$\text{Fe}_3\text{O}_4/\text{CeO}_2$	100	1	120	2×10^{-2}	(Li et al. 2017a)
$\text{Fe}_3\text{O}_4/\text{galic acid}/\text{GO}$	64	1	200	1.2×10^{-2}	(Hua et al. 2017)
$\text{N,C}/\text{CuO}-\text{Fe}_2\text{O}_3$	75	0.1	180	1.08×10^{-2}	(Ren et al. 2019)
$\text{FeNi}/\text{C}-300$	30	1	30	1.05×10^{-2}	(Li et al. 2020)

352

353 4 Conclusions

354 An iron ore tailings-based Fenton-like catalyst(I/W(3:1)-900-60) with relative fast
 355 catalysis rate was constructed by co-pyrolysis($900 \text{ }^\circ\text{C}$, 60min holding time) of iron ore

356 tailings and wheat straw with mass ratio of 3:1. Compared with single pyrolyzed iron
357 ore tailing, the catalytic efficiency and rate of I/W(3:1)-900-60 (0.0229 min^{-1} , 84%)
358 were considerably enhanced for the decomposition of MB due to the electron transfer
359 between biochar and iron active sites or the redox cycles of $\equiv\text{Fe}^{3+}/\text{Fe}^{2+}$. As a result of
360 the sacrificial effect of biochar, oxidizing $\text{C}=\text{Csp}^2$ bonds and limiting the deactivation
361 of iron active sites($\equiv\text{Fe}^{2+}$), I/W(3:1)-900-60 showed a good reusability and stability.
362 Moreover, the presence of unpaired electrons in persistent free radicals (PFRs) of
363 biochar accelerated the electron exchange and further enhanced the MB decomposition
364 rate. This work opens up a way to synthesize an iron ore tailings-based Fenton-like
365 catalyst with higher degradation rate, as well as realize the utilization of solid wastes.

366

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370 **Author contributions**

371 Lihui Gao: Writing-original draft, methodology, Data curation; Lizhang Wang:
372 Writing-Reviewing and Editing; Shulei Li: Investigation, Sample preparation; Yijun
373 Cao: Supervision and Editing.

374 **Availability of data and materials:** All data generated or analyzed during this
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